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(21) International Application Number: PCT/US86/01875 (22) International Filing Date: 12 September 1986 (12.09.86) (31) Priority Application Number: 789,887 (32) Priority Date: 21 October 1985 (21.10.85) (33) Priority Country: US (71) Applicant: OWENS-CORNING FIBERGLAS CORPORATION [US/US]; Fiberglas Tower 26, Toledo, OH 43659 (US). (72) Inventors: BRANNON, Robert, Clifford ; 613 Moull Street, Newark, OH 43055 (US). COLEMAN, David, Alan ; 53 Edgemill Drive, Newark, OH 43055 (US). MILLER, David, George ; 42 Aspen Lane SW, Pataskala, OH 43062 (US).	(74) Agents: HUDGENS, Ronald, C. et al.; Fiberglas Tower 26, Toledo, OH 43659 (US). (81) Designated States: AU, BE (European patent), DE (European patent), FR (European patent), IT (European patent), JP, NL (European patent). Published <i>With international search report.</i>	

(54) Title: POLYESTER EMULSION**(57) Abstract**

A cure stable polyester emulsion for use in an aqueous size composition has been developed for glass fibers produced for molded products having appearance surfaces known as Class A surfaces. The emulsion consists essentially of an unsaturated polyester resin emulsified with nonylphenoxy poly (ethyleneoxy) ethanol. The size contains this cure stable unsaturated polyester emulsion and a static insensitive lubricant system. The resulting coated glass fibers are especially useful in improving processability and product uniformity of SMC application.

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D E S C R I P T I O N
POLYESTER EMULSION

10

TECHNICAL FIELD

This invention relates to polyester emulsions.

The emulsions are intended for size compositions for glass fibers which may be incorporated into molding compounds.

BACKGROUND ART

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The use of unsaturated polyester compounds in combination with thermoplastic resins and fillers to produce molding compositions is well known. These compositions, intended to polymerize when molded under heat and pressure, are generally combined with fillers and chopped glass, produced from roving, to produce molded products having appearance surfaces with a minimum of irregularities or undulations known as Class A surfaces.

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The use of chopped glass as reinforcement in such molding compounds is well known. The chopped glass is produced in the form of individual strands which are sized, gathered into rovings, chopped to the desired length and incorporated into the resin composite prior to molding.

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The sizes generally comprise a polyester emulsion base, a lubricant, film formers and the like and are extremely important in imparting to the reinforcing glass its ability to be wetted out by the molding compound. These sizes are also important in that they protect the glass in its handling subsequent to being sized and are influential in minimizing the amount of fuzz and fly which is produced

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on the glass, the fuzz and fly having a decided affect upon the appearance surface of the molded product.

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1 The sized glass fibers generally are employed as reinforcement for sheet molding compounds (SMC) and bulk molding compounds (BMC).

DISCLOSURE OF INVENTION

5 According to this invention, we have provided an improved polyester emulsion for polyester-based sizes. We have a cure stable polyester emulsion for these sizes. The resulting formulation provides for very low static generation which allows antistatic methods to work better
10 even at low relative humidity. The sized glass fibers are particularly suitable for use in sheet molding compounds.

Unsaturated polyesters useful in this invention typically contain a polyesterification product of one or more ethylenically unsaturated dicarboxylic acids or
15 anhydrides such as maleic or fumaric with one or more glycols such as ethylene or propylene glycol and, sometimes, minor proportions of other aromatic or aliphatic mono- or dicarboxylic acids or anhydrides and/or other mono- or polyhydroxyl compounds. They also typically contain an
20 ethylenically unsaturated monomer, such as styrene, copolymerizable with the unsaturated polyester for curing.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a graph showing surfactant stability as measured by isothermal thermogravimetric weight loss.

25 FIG. 2 is a graph showing acetone solubility through the forming cake.

FIG. 3 shows electrostatic data obtained from the size of Example 1.

30 FIG. 4 shows electrostatic data obtained from the control size of Example 2.

BEST MODE OF CARRYING OUT THE INVENTION

The unsaturated polyesters are primarily polyesterification products of an ethylenically unsaturated dicarboxylic acid or anhydride such as maleic acid or
35 anhydride (which will ordinarily and preferably be at least partially isomerized to the fumarate form during the polyesterification) and a glycol such as ethylene or

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1 propylene glycol or the corresponding epoxide. Minor molar
proportions of other acid and/or hydroxyl reactants can be
incorporated, if desired, according to generally accepted
practice. For example, the reactivity of the polyester in
5 the addition copolymerization reaction involved in curing
can be reduced by substituting a dicarboxylic acid or
anhydride not having any ethylenic unsaturation for a minor
molar proportion of the ethylenically unsaturated
dicarboxylic acid or anhydride. Either aliphatic or
10 aromatic substitutes may be employed, the most common
probably being isophthalic acid. Minor molar proportions of
monofunctional carboxylic acid or alcohol reactants can also
be incorporated; these can serve not only to modify the
reactivity of the resultant polyester and its compatibility
15 with other size components but can also be employed to
control its acid and/or hydroxyl value independently of its
average molecular weight.

The cure stable polyester emulsion is a
conventional unsaturated polyester emulsified with
20 nonylphenoxy poly (ethyleneoxy) ethanol. One such material
is Igepal CO-997 from GAF. This surfactant does not degrade
during drying and does not interfere with the cure of the
polyester resin.

This invention may be used in an aqueous size
25 composition comprising, approximately, on a weight percent
basis:

	<u>Weight Percent</u>
Cure, stable polyester emulsion	50 - 55
Polyvinylacetate copolymer	40 - 45
30 Glacial acetic acid	0 - 0.3
Silane	2 - 4
Static insensitive lubricant	0.05 - 2
Wax	0 - 3
Water	Balance
35 Final solids content ranges from 10 to 15 percent. The sizing composition is applied so as to deposit a dried size	

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1 coating on the fibers corresponding to about 0.2 to 3.0 weight percent of the weight of the fibers (LOI).

Preferably, the size composition is prepared according to the following formulation:

		<u>Weight Percent</u>
5	Cure, stable polyester emulsion	51.5 - 53.5
	Polyvinylacetate copolymer	41.5 - 43.5
	Glacial acetic acid	0 - 0.3
	Silane	2 - 3
10	Static insensitive lubricant	0.05 - 1
	Wax	0 - 2
	Water	Balance

Preferably, final solids content ranges from 11 to 14 percent. The sizing composition is applied so as to deposit 15 a dried size coating on the fibers corresponding to about 0.2 to 2 weight percent of the weight of the fibers (LOI).

The control resin used in the following examples is a conventional unsaturated polyester emulsified with a block co-polymer of polyoxyethylene and polyoxypropylene.

20 One such material is Pluronic^R F-77 from BASF.

Both the cure stable polyester emulsion of this invention, CX1717 from Owens-Corning Fiberglas, and the control polyester emulsion of Example II, CX412 from Owens-Corning, are prepared from Owens-Corning E-400 25 polyester resin. E-400 is a conventional polyester resin prepared from phthalic anhydride (26%), maleic anhydride (17%), propylene glycol (28%) and styrene (27%). The balance being CO-997 for the present invention versus F-77 for the control emulsion, and very small amounts of 30 toluhydroquinone and p-benzoquinone inhibitors.

The emulsification procedure that was used is as follows. The E-400 resin is charged to a mixer fitted with a chiller. The chiller is turned on before the resin is charged. Next, the surfactant (emulsifier) is added. 35 Igepal CO-997 must be heated to a pourable liquid before adding. The resin and surfactant are mixed for 1 hour at a high shear of 700 and a sweep of 10. Water addition then is

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1 carried out to achieve a desired solids content. After
process is complete, allow batch to mix ten (10) minutes
then take sample for particle size and solids. Solids and
viscosity are finally adjusted by water addition. When
5 batch is in specification, sample is ready.

The static insensitive lubricant is a combination
of cocoa amine acetate and a polyethyleneimine. We selected
this chemistry to obtain low fuzz during SMC processing
without affecting cure of the polyester or PVAC film
10 formers.

The pH of the size typically ranges from 2 to 4
and preferably is about 3.

Example I

A size composition using the inventive polyester
15 emulsion was prepared from the following ingredients.

	<u>Weight Percent</u>
Cure stable polyester emulsion; CX1717 from Owens-Corning Fiberglas	52.31
Polyvinylacetate copolymer; National Starch 25-2828	42.80
Gamma-methacryloxy- propyltrimethoxysilane; Union Carbide A-174	2.94
Cocoa amine acetate; Alkaril PF-710	0.25
Polyethyleneimine; Emery 6760u	0.25
Carbowax; Union Carbide C-1000	1.45
Deionized water	Balance
35 Final solids content was about 14 weight percent. The sizing composition is applied so as to deposit a dried size	

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1 coating on the fibers corresponding to about 2 weight percent of the weight of the fibers (LOI).

Example II (Control)

A control size composition was prepared from the 5 following ingredients.

		<u>Weight Percent</u>
	Conventional polyester emulsion;	64.33
	Owens-Corning Fiberglas 412	
10	Polyvinylethylene emulsion; Air Products A400	15.20
	Polyvinylacetate copolymer; National Starch 25-2828	13.98
15	Gamma-methacryloxy- propyltrimethoxysilane; Union Carbide A-174	2.85
20	Cirrasol 185AEAN pelargonic acid and tetraethylenepentamine	2.22
	Carbowax; Union Carbide C-1000	1.41
25	Deionized water	Balance

The percent solids in the size composition was about 13. The strand solids corresponded to about 2 weight percent of the weight of the fibers (LOI).

INDUSTRIAL APPLICABILITY

30 Example III

The size of Example I and the control size of Example II were prepared by conventional size preparation methods and applied to the glass strand using conventional application techniques. The incorporation of the sized 35 strands into the resin composition is performed by conventional methods.

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1 Glass fibers used in the practice of this
invention can be, but are not restricted to, "E" glass
fibers, well known to those skilled in the art. Such fibers
are described in U.S. Patent No. 2,334,961.

5 Strands of glass fibers are produced by pulling
several hundred or more tiny molten streams of glass which
issue from holes in the bottom of a bushing over a size
applying apron to a gathering shoe which groups the fibers
together into a strand. This strand then proceeds to a
10 traverse mechanism and winding drum which provides the
pulling action which attenuates the molten glass and coils
the strand into a package. The fibers are individually
separated at the time that they pass over the size
applicator, so that the surfaces of the fibers are
15 substantially completely coated before they are drawn
together into a strand. This size acts as a lubricant which
separates the individual filaments, and if the filaments are
not separated by the size, they will scratch each other and
break as they are flexed and drawn over guide eyes or other
20 contact surfaces in subsequent operations such as roving or
SMC compounding.

Example IV

Glass fibers coated with the size of Example I and
the control size of Example II were compared as follows.

25 FIG. 1 shows the thermal stability in air of
Igepal^R CO-997 vs. control F-77 surfactant. The inventive
surfactant only loses about 8 to 10% solids over 17.5 hours
at 130°C (265°F). The control surfactant lost about 92%
solids under the same conditions.

30 FIG. 2 shows the acetone solubility for the sized
glass fibers of this invention vs. the control product dried
over 13 hours at 130°C (265°F). The inventive size
consistently had lower solubility at various positions
through the forming cake. Consistency of cure through the
35 forming cake is due to the improved thermal stability of
CO-997 surfactant relative to F-77. The forming cakes are
terms used to identify strands of sized glass fibers prior

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1 to further finishing operations. The effectiveness of the
Igepal^R surfactant in controlling solubility and cure of the
polyester film former is apparent from this data.

Electrostatic properties were obtained on forming
5 cakes made from each of the sizes in Examples I and II. In
this test, a single strand from a forming cake is
triboelectrically charged by a constant friction device and
monitored for residual charge with an electrostatic probe.
Both generation and dissipation mechanisms are characterized
10 by this method. The monitored charge is converted to a
relative frequency histogram, which includes several strands
from the same forming cake.

The static data for Examples I and II are shown in
Figures 3 and 4, respectively. The inventive product
15 reduces the amount of highly charged negative surface
potential. This results in a more narrow charge
distribution and a nominal charge which is closer to zero.
Both of these factors improve static performance during SMC
processing. Static buildup on chopper surfaces is reduced,
20 and uniformity of the chopped glass bed is improved.

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C L A I M S

1. Cure stable polyester emulsion consisting
10 essentially of an unsaturated polyester resin emulsified
with nonylphenoxy poly (ethyleneoxy) ethanol.
2. Polyester emulsion according to claim 1 having
an amount of the ethanol ranging from 2 to 20 weight percent
based on the weight of resin.
- 15 3. Polyester emulsion according to claim 1 having
an amount of the ethanol ranging from 2 to 5 weight percent
based on the weight of resin.
4. Polyester emulsion according to claim 1
wherein the polyester resin comprises ethylenically
20 unsaturated polyester and ethylenically unsaturated monomer
copolymerizable with the polyester.
5. Polyester emulsion according to claim 4
wherein the unsaturated polyester is prepared from
ethylenically unsaturated dicarboxylic acid or anhydride and
25 glycol or corresponding epoxide.
6. Polyester emulsion according to claim 4
wherein the polyester resin is prepared from phthalic
anhydride, maleic anhydride, propylene glycol and styrene.

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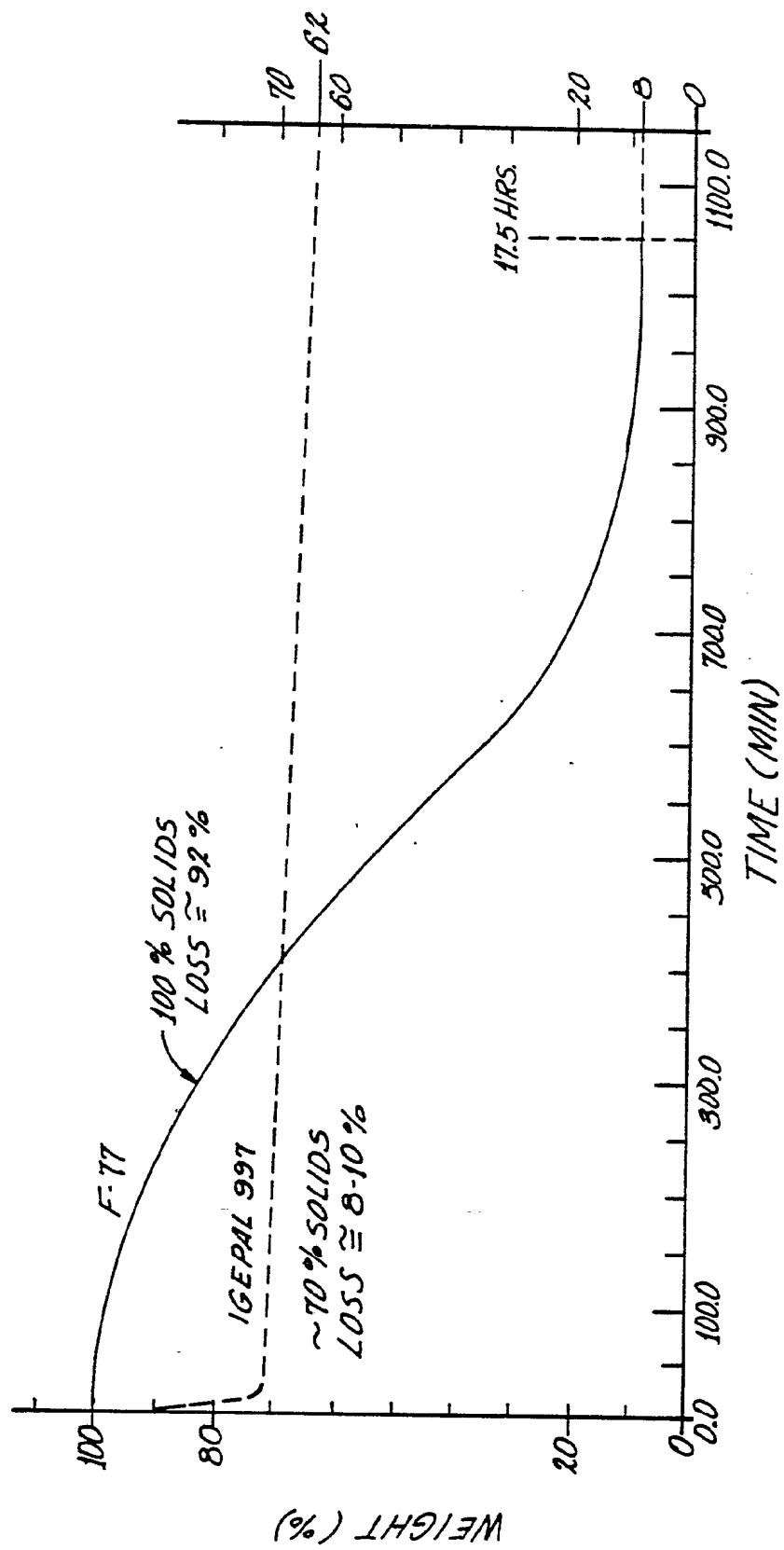
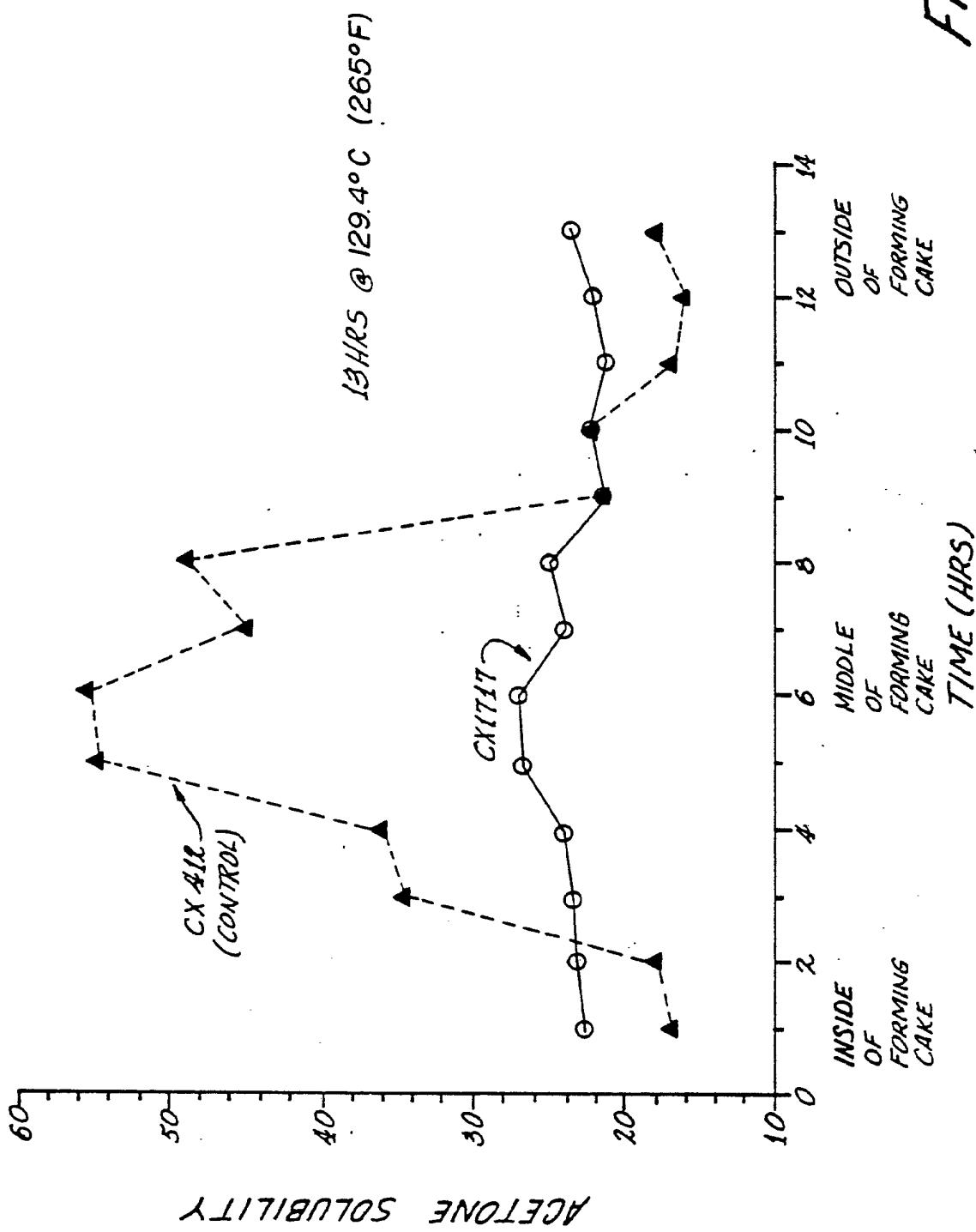


FIG.1

SURFACTANT STABILITY

FIG. 2



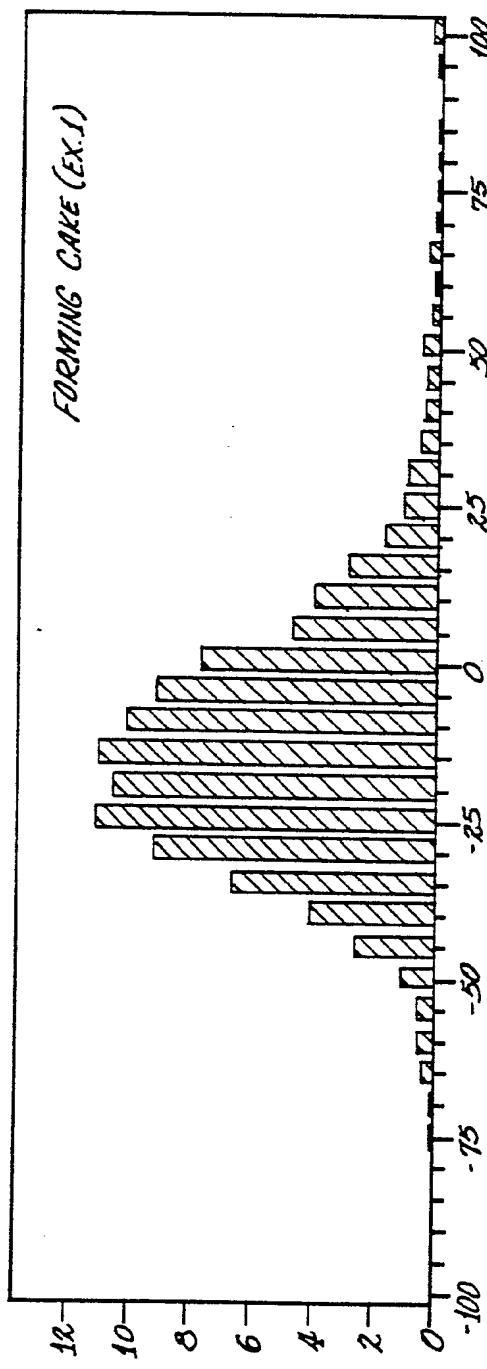


FIG. 3

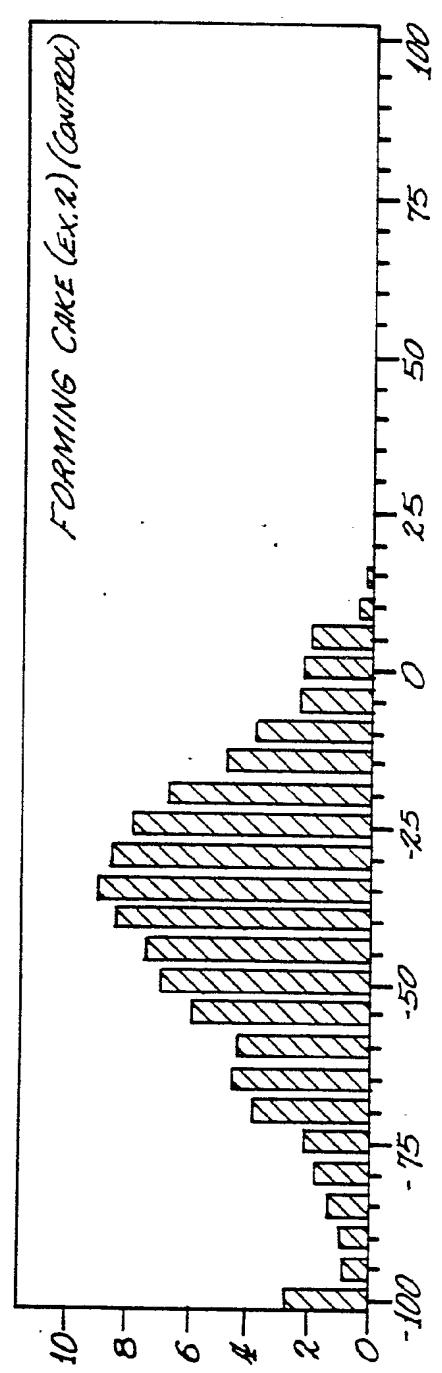


FIG. 4

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US 86/01875

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC ⁴ : C 08 F 299/04; C 08 J 3/10; C 08 L 67/06; // C 03 C 25/02		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
IPC ⁴	C 08 F; C 08 J; C 08 L; C 03 C; D 06 M	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT*		
Category ⁹	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
P, X	EP, A, 0181839 (SOGIMI) 21st May 1986, see claims 1-10; page 6, lines 8-16; examples 4-9 --	1-6
X	US, A, 3440193 (P.J. CAMPAGNA) 22 April 1969, see column 2, lines 3-35; column 3, line 3 - column 4, line 2; column 4, lines 17-57; examples 1-10 --	1-3
X	DE, A, 2903022 (BAYER) 31 July 1980, see claims --	1-3
A	GB, A, 1434448 (OWENS-CORNING FIBERGLAS) 5 May 1976 -----	
<p>* Special categories of cited documents:¹⁰ "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "A" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
4th December 1986	21 JAN 1987	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	J. VAN MOL 	

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON

INTERNATIONAL APPLICATION NO. PCT/US 86/01875 (SA 14541)

This Annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 11/12/86

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A- 0181839	21/05/86	None	
US-A- 3440193	22/04/69	NL-A- 6606104 BE-A- 680595 FR-A- 1478892	07/11/66 17/10/66
DE-A- 2903022	31/07/80	None	
GB-A- 1434448	05/05/76	None	